

OXIDATIVE COUPLING OF METHANE OVER
RARE-EARTH-BASED NONREDUCIBLE COMPOSITE-METAL-OXIDES CATALYSTS¹

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ABSTRACT

Nonreducible composite metal-oxides catalysts of the host-dopant type can be very effective catalysts for methane oxidative coupling (MOC) reaction(s) and for oxidative dehydrogenation of ethane to ethene. A systematic study of the relative efficacies of the alkali and alkaline-earth dopants used as selectivity promoters for lanthania-based MOC catalysts in relation to the cationic polarizabilities, and of the behavior of a CsOH-coated lanthania catalyst towards treatment with CO₂ plus O₂ near the MOC reaction temperature and toward CO₂-containing feeds has been made, together with laser Raman spectroscopic detection of superoxide ions in the freshly activated catalyst. The results strongly indicate that O₂⁻ adspecies is an active oxygen species responsible for the initial alkane-hydrogen-abstraction reactions.

INTRODUCTION

Methane oxidative coupling (MOC) over solid catalysts is of great current interest because of its potential importance in the utilization of the world's abundant natural gas resource for the production of ethylene or liquid fuels, and of its fundamental significance in the catalytic activation and selective conversion of the first and the most inert member of paraffin hydrocarbons. Much attention has been focused on the development of better catalysts for the MOC reaction(s) and on mechanistic studies of O₂ activation and methane conversion; and important advances have been made since the pioneering work of Keller & Bhasin [1], as shown by many recent reviews [2].

The great number of MOC catalysts reported in the literature may be roughly classified into three main categories (1) nonreducible composite metal-oxides with stable cationic valency; (2) basic-oxide-supported catalysts of reducible oxides of certain IVA, VA metals, e.g., PbO_x, Bi₂O_x, or oxides of certain IIb-elements (Zn and Cd); and (3) alkali-oxides (or phosphates or sulfates or chlorides)-promoted complex catalysts containing oxides of certain transition metals, e.g., MnO_x, TiO_x, MoO_x, and the recently reported CaO-NiO-K⁺ [3].

MOC catalysts of the first category are the most extensively investigated. These are usually of the host-dopant type, each consisting of a host oxide of a higher-valent cationic metal from the IIA or IIIB or IVB group doped with one or more basic oxides with lower and stable cationic valency from the IA, or IIA or IIIB group so as to generate or increase lattice anionic vacancies, which appear to be requisite for dioxygen chemisorption and activation. However, the IIA-IA

¹ Work supported by the National Natural Science Foundation of China and by a grant for spectroscopic characterization from the State Key Laboratory for Physical Chemistry of The Solid Surface, Xiamen University.

catalyst systems all suffer from the serious drawback of high volatilization loss of the alkali promoters and significant sintering at the MOC reaction temperature [2,3a]. The use of high-melting trivalent or quadri-valent metal oxides with stable cationic valency, such as alkaline-earth oxides (AEO) and/or oxides of IIIB metals, especially the M_2O_3 -type rare-earth-oxides (REO), many of which are known [4] to exist in the cubic C-type structure, a defective fluorite structure with regular disposition of anionic vacancies (e.g., Sm_2O_3). As pointed out in references [5-6], these REO with the C-type structure or layer-type structure (e.g., La_2O_3) are extremely open to oxygen chemisorption. These REO, especially Sm_2O_3 , have been found to show very high oxygen conversion efficiency and fairly good MOC activity and selectivity [2,7,8], but Sm_2O_3 appears to have only marginal C-type structural stability at the MOC reaction temperature [3a]. Doping La_2O_3 and Sm_2O_3 catalysts with small amounts of alkali or AEO has been found to enhance \dot{C}_2 selectivity [2,3a,6-8], but the results from different investigators are not very consistent. It is known [9] that metal oxides with the fluorite structure (notably ThO_2) can form wide ranges of solid solutions with many M_2O_3 -type REO, and can also dissolve AEO to some extent, especially when the host-dopant cationic sizes are comparable. Thus defective-fluorite-structure (DFS) with high concentration of anionic vacancies can be created by proper doping of the fluorite-type host-oxides with metal-oxides of lower cationic valency. As recently shown by Cameron et al. [10], such dopings can radically change the low-activity ThO_2 host-oxide into very active and selective MOC catalysts for the co-feed operation. For the nonreducible composite metal-oxides, the active site for the initial alkane-hydrogen-abstraction reaction is most probably certain chemisorbed oxygen species, the very nature of which is still not clear, and remains a matter of controversy [2,6,10-12]. The mechanism of promoter action of the alkali and AEO dopants also remains to be clarified.

In this paper, further experimental evidence for the catalyst activities and selectivities in relation to structural types and anionic vacancies for this category of MOC catalysts is first presented; this is followed by presentation and discussion of the results of a systematic study of the relative efficacies of the alkali and AEO promoter in relation to the cationic polarizabilities, and of the behavior of a CsOH-coated La_2O_3 catalyst towards treatment by CO_2 plus O_2 , as well as towards CO_2 -containing feeds, together with detection of anionic-dioxygen species in the freshly activated catalyst, with the aim of shedding some light on the nature of the active oxygen species and the mechanism of the promoter action.

EXPERIMENTAL

Catalyst Preparation, Evaluation, and Characterization

Undoped La_2O_3 , Y_2O_3 , ZrO_2 , and ThO_2 , as well as the $[Y_2O_3]ZrO_2$ (35 mol.% Y:65 mol.% Zr), $[La_2O_3]ThO_2$ (30 mol.% La:70 mol.% Th), and $pSm_2O_3]ThO_2$ (30 mol.% Sm:70 mol.% Th) host-dopant pairs, the Bi_2O_3 -doped $[La_2O_3]ThO_2$ catalyst (10 mol.% Bi:20 mol.% La:70 mol.% Th), and the AEO-doped (5 mol.% M^{2+} in each case) La_2O_3 catalysts were prepared by drying and ignition (830-900°C, 1 hr) of freshly precipitated, or co-precipitated hydroxides, or carbonates in the case of the AEO-doped La_2O_3 catalysts, while the alkali-sulfates-doped La_2O_3 catalysts (5 mol.% M in each case) and the CsOH-coated lanthania catalyst (10 mol.% Cs:90 mol.% La) by impregnation of ignited lanthania with the aqueous metal sulfates and CsOH, respectively, followed by drying and ignition (700°C).

Catalyst evaluation was carried out in a quartz microreactor (6.0 mm i.d. with concentric quartz tubing serving as thermal-couple well)-G.C. (TCD) outfit, 0.20 mL of catalyst sample (30-60 mesh) being used in each case. The feed ($CH_4:O_2:N_2 = 24.6:5.6:69.8$ vol.% being used throughout this work) and the reactor effluents were analyzed with a gas chromatograph

(Shanghai Fenxi, Model #103) equipped with thermal conductivity detector, a molecular-sieve-5A column, as well as a Porapak-Q column, being used to separate O_2 , N_2 , CH_4 , and CO , as well as CO_2 , C_2H_4 , and C_2H_6 (C_3+ and H_2O being neglected), respectively, and N_2 as the internal reference for the quantitation of each gaseous component from its G.C. peak. The selectivity for each C-containing product and the ΣC_2 yield were expressed in terms of the carbon-efficiency (%) of methane conversion to the respective product. In each case, a $95 \pm 2\%$ carbon material balance was obtained. Laser Raman spectra for freshly activated sample of the CsOH-coated La_2O_3 catalyst and for partially deactivated sample, as well as for freshly prepared sample (ignited at $700^\circ C$ for 1 hour in ambient air) before the activation treatment, were taken at room temperature with a Spex Ramalog-6 spectrometer with argon laser (5145 \AA) as the excitation source.

RESULTS AND DISCUSSION

Catalyst Performance in Relation to Compositions and Structural Peculiarities

The experimental results show that doping ThO_2 with a trivalent-lanthanide oxide (La_2O_3 and Sm_2O_3 appeared to be equally effective), or ZrO_2 with Y_2O_3 , to produce a composite metal oxide with defective fluorite structure (DFS) can be very effective in changing a poor MOC catalyst with no intrinsic anionic activity and, especially selectivity (Table 1), in accordance with observations by previous workers [10]. Note that these DFS metal-oxides are known to be solid electrolytes with high anionic conductivities, especially the zirconia-yttria system [9]. It is interesting to note that the 10 mol.% Bi_2O_3 -doped $[La_2O_3]ThO_2$ catalyst appeared to be a highly efficient methane-combustion catalyst, rather than a MOC catalyst. Conceivably, the presence of the redox-active Bi (III/IV) in the DFS lattice of $[La_2O_3]ThO_2$ can promote the reductive dissociation of O_2 ($O=O$ bond energy: 118 kcal) chemisorbed at an anionic vacancy into $2O^-$, most probably via the formation of O_2^{2-} (ionic 'O-O' bond energy: 34 kcal) as precursor; and high concentration and mobility of O^- in the catalyst may be conducive to deep oxidation of CH_4 (C_2H_6 and C_2H_4), and detrimental to MOC selectivity. Incidentally, doping a [25 mol.% $LaO_{1.5}$] ThO_2 with 5 mol.% PbO was also found to promote CO_2 formation (64% CO_2 , 36% C_2).

Table 1
Catalyst Activity and Selectivity in Relation to Structural Peculiarities

Catalyst System Composition	Structure Type	Reaction Temp. ($^\circ C$)	GHSV (h^{-1})	Conversion		Selectivity C_2 (%)
				CH_4 (%)	O_2 (%)	
ThO_2	Fluorite	760	12×10^4	11	34	42
30 mol.% $SmO_{1.5}$ - ThO_2	DFS	760	12×10^4	27	95	57
30 mol.% $LaO_{1.5}$ - ThO_2	DFS	760	12×10^4	28	94	55
$BiO_{1.5}$ - $LaO_{1.5}$ - ThO_2 (10 : 20 : 70)	DFS	700	12×10^4	13	98	0 (100% CO_2)
ZrO_2	Monoclinic	760	3×10^4	19	98	7
Y_2O_3	C-type	760	3×10^4	26	98	38
35 mol.% $YO_{1.5}$ - ZrO_2	DFS	760	3×10^4	26	92	46

Promoter Effects of Alkali Sulfates and Alkaline-Earth Oxides on La_2O_3 Catalyst

The promoter effects were found to increase with increasing cationic sizes:



This may be correlated to the increasing tendencies towards the formation of the corresponding metal-superoxides [13-14], which, in turn, may be correlated to the increasing cationic polarizabilities [15]. Conceivably, by acquiring an electron trapped at an anionic vacancy, or from an O^{2-} ion, an O_2^- adspecies may be formed from a chemisorbed O_2 ; likewise, O_2^{2-} adspecies may then be formed by acquiring a second electron. The O_2^{2-} adspecies may dissociate reversibly into 2 O^- , which may readily diffuse into the bulk. The half-life of anionic dioxygen adspecies, especially O_2^- , may be prolonged by side-on coordination [14] to a highly polarizable dopant cation (e.g., Cs^+ , Rb^+ , or K^+) known to have a strong tendency to form metal superoxide [12-13], which, however, is very sensitive to inhibition by moisture [14], due to conversion into the highly soluble and thermally very stable alkali hydroxide (with the exception of $LiOH$, which is barely soluble in water, and dehydrates to Li_2O at $850^\circ C$ [4b]). Note that the promoter effects of the alkali sulfates, with the notable exception of Li_2SO_4 , all appeared to decrease rapidly with time on stream. However, the promoter effect of Na_2SO_4 taken in the first 30 minutes to an hour was reproducibly found to be slightly better than that of Li_2SO_4 (Table 2).

Table 2
Promoter Effects of Alkali Sulfates and AEO on La_2O_3 -Based Catalysts

Catalyst (mol.%)	Temp. ($^\circ C$)	GHSV (h^{-1})	Conversion (%)		Selectivity (% Efficiency)		
			CH_4	O_2	C_2H_6	C_2H_4	ΣC_2
5% Li^+/La_2O_3	700	1.5×10^4	29.4	85.8	29.5	31.0	60.5
5% Na^+/La_2O_3	700	1.5×10^4	28	83	29	33	62
5% K^+/La_2O_3	700	1.5×10^4	29	80	30	35	65
5% Rb^+/La_2O_3	700	1.5×10^4	30	89	33	35	68
5% Cs^+/La_2O_3	700	1.5×10^4	29	80	34	36	70
La_2O_3	700	3.0×10^4	28.1	99.0	24.6	25.3	49.9
5% Mg^{2+}/La_2O_3	700	3.0×10^4	28.6	97.8	26.2	25.6	51.8
5% Ca^{2+}/La_2O_3	700	3.0×10^4	27.9	98.0	27.1	25.6	52.7
5% Sr^{2+}/La_2O_3	700	3.0×10^4	28.0	98.1	30.4	24.8	55.2
5% Ba^{2+}/La_2O_3	700	3.0×10^4	28.9	98.1	32.6	26.5	59.1

Effects of CO_2 Treatment and of CO_2 in Feed on $CsOH$ -Coated Lanthania Catalyst

The 10 mol.% $CsOH/La_2O_3$ catalyst was found to behave like molten $CsOH$ (ca. 25-30 Å thick) supported on La_2O_3 (4 m²/g). The MOC activity and selectivity were again found to decline rapidly with time on stream (Table 3), most probably also due to inhibition by H_2O coproduced in the MOC reactions; but the ΣC_2 selectivity was increased with the addition of 4-5 vol.% of CO_2 into the feed, though with a slight depression in the CH_4 conversion. Moreover, the catalyst could be reactivated by treatment with CO_2 plus a few percents of O_2 . Laser Raman spectrum of the freshly activated sample taken at room temperature indicated the presence of a large amount of carbonate (1086 cm^{-1} st, 700 cm^{-1} w), a small amount of CsO_2 (1128 cm^{-1} w, plus some weak, unresolved and unidentified peaks around $980\text{--}1000\text{ cm}^{-1}$), the assignments of the Raman peaks being made with reference to [15-16]. After 3 hours on stream, only the large carbonate-peak at 1086 cm^{-1} remained; the peak assignable to CsO_2 being no longer visible. The spectroscopic characterization will be communicated in more details later. Conceivably, molten $CsOH$ can readily absorb CO_2 to form Cs_2CO_3 (d. $610^\circ C$ [4b]), which is readily decarbonated at $700^\circ C$ to form Cs_2O , which in turn can readily absorb O_2 to form, predominantly, CsO_2 [13], plus a small amount of Cs_2O_2 ; both of these may dissolve in the molten $CsOH$, and appear to be not so active and selective as compared with the previous case

of 5 mol.% $\text{Cs}_2\text{SO}_4/\text{La}_2\text{O}_3$ where O_2^- adspecies was probably partially stabilized by Cs^+ dopant cations incorporated into the surface lattice of La_2O_3 during the impregnation and heat treatment.

Table 3
Effects of CO_2 - O_2 Treatment and of CO_2 in the Feed on 10 mol.% $\text{CsOH}/\text{La}_2\text{O}_3$ Catalyst

Time (min.) on Stream	Feed or Reagent	Temp. (°C)	Conversion (%) ^a		Selectivity (%) ^a			$\text{Y}\Sigma\text{C}_2^a$ (%)
			CH_4	O_2	C_2H_6	C_2H_4	ΣC_2	
0-30	Feed	700	27.8	94.7	30.1	23.9	54.0	15.0
30-150	Same	700	27.4	94.7	27.2	22.5	49.7	13.6
150-250	Same	700	26.4	95.8	26.5	21.9	48.4	12.8
250-310	$\text{CO}_2 + 2\% \text{O}_2$	700						
310-335	Feed	700	28.5	95.9	28.5	25.2	53.7	15.3
335-400	Feed+5% CO_2	700	27.5	99.0	90.8	38.5	55.0	15.1
400-430	Feed	700	28.9	93.8	26.6	23.8	50.0	14.6
430-460	Feed+4% CO_2	700	27.8	93.6	27.8	25.2	53.0	14.7

Feed: $\text{CH}_4:\text{O}_2:\text{N}_2 = 24.6:5.6:69.8$ (vol.%). GHSV: $2 \times 10^4 \text{h}^{-1}$. ^aData taken at the end of the time interval.

Thus the results of the last two sections strongly indicate that O_2^- adspecies, is an active-oxygen species responsible for the initial alkane-hydrogen-abstraction in the MOC reactions (and in oxidative dehydrogenation of ethane). This is in line with the known experimental fact that this step requires a fairly large activation energy [2.12a], and that significant amounts of O_2^- adspecies, rather than O^- and O_2^{2-} species, are present in the great majority of efficient MOC co-fed catalysts. These findings have important bearings on the design of MOC catalysts and operating conditions.

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